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COMPLETE SPECIFICATION

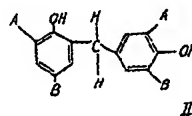
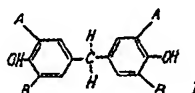
Asymmetric Methylene-Bis-Phenols and their use as Anti-Oxidants

We, ETHYL CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100 Park Avenue, New York 17, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phenolic antioxidants and more particularly to asymmetric phenolic compounds having outstanding antioxidant properties in a wide variety of organic media.

Certain methylene-bis-phenols have been shown to be outstanding antioxidants in a variety of organic media, although ordinarily the antioxidant activity varies considerably from medium to medium. For example, some compounds are outstanding antioxidants for mineral lubricating oils while closely related compounds are found to have outstanding properties as antioxidants in various forms of polyethylene. By testing the compounds in the two media, it can be shown that because a compound has outstanding effectiveness in polyethylene, for example, does not mean it will be particularly remarkable in lubricating oils. Thus, minor changes in the structure of a phenolic antioxidant greatly affect its antioxidant activity from one medium to another. This causes a considerable inconvenience to the manufacturer and user of antioxidants in that it is necessary to prepare different compounds to obtain maximum antioxidant efficiency in a given medium.

According to the invention we provide asymmetrical methylene-bis-phenols having the general formula:



wherein

A and B are hydrogen atoms or alkyl groups having up to 9 carbon atoms and wherein at least one A or B is a tertiary alkyl group having from 4 to 9 carbon atoms and is positioned ortho to one of the hydroxyl groups, and when the hydroxyl groups are both para to the methylene bridge A and B are such that the molecule is not symmetrical.

In formula II, it is preferred that A and B be tertiary alkyl, particularly tertiary butyl.

We also provide a process of preparing asymmetric methylene-bis-phenols having the above formulae (in admixture with symmetrical methylene bis phenols compounds) which comprises reacting a mixture of mono-nuclear phenols with formaldehyde and an aliphatic alcohol, said mixture containing at least one phenol having an available hydrogen in the ortho or para position and at least one phenol having a tertiary alkyl group ortho to the hydroxyl group and also an available hydrogen

in the ortho or para position, the reaction being carried out under basic conditions. The most preferred compound of this invention is (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane. It has been found that this compound has outstandingly fine antioxidant activity in a wide variety of oxygen-sensitive organic material. It has further been found that methods of preparing this compound are available which give rise to a liquid composition readily soluble to a high extent in such liquid organic compositions as mineral lubricating oils and functional fluids.

Representative compounds of this invention which correspond to Formula I above include: (3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-(4¹-hydroxyphenyl)-methane, (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(4¹-hydroxyphenyl)-methane, (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3¹,5¹-di-methyl-4¹-hydroxyphenyl)-methane, (3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-(3¹-methyl-4¹-hydroxyphenyl)-methane, (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3¹-methyl-4¹-hydroxyphenyl)-methane, (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-methyl-5-*tert*-amyl-4-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, and [3-(1¹,1¹,3¹,3¹-tetramethylbutyl)-5-methyl-4-hydroxyphenyl]-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane.

Illustrative of compounds having the structure shown in Formula II above include: (3-*tert*-butyl-2-hydroxyphenyl)-(3,5-di-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-*tert*-butyl-2-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, (2-hydroxyphenyl)-(3¹,5¹-di-*tert*-butyl-4¹-hydroxyphenyl)-methane, (2-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-methyl-2-hydroxyphenyl)-(3¹,5¹-di-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-methyl-2-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, (3-methyl-5-*tert*-butyl-2-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane, and (3-methyl-5-*tert*-butyl-2-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane.

One method of preparing the compounds of this invention comprises reacting a mixture of mononuclear phenolic compounds with formaldehyde in the presence of a lower aliphatic alcohol having up to 4 carbon atoms under basic conditions. In this reaction the mixture of phenols contains at least one phenol having a hydrogen atom available in an ortho or para position and at least one phenol containing a tertiary alkyl group ortho to the

hydroxyl group and which also contains one ortho or para hydrogen.

Thus, when it is desired to prepare a compound of Formula I, a mixture of a 2,6-dialkylphenol in which one of the alkyl groups is a tertiary alkyl group and an alkyl phenol having a hydrogen in the 4-position such as 2,6-xilenol is used. A compound of Formula II can be prepared, for example, by the reaction between 2,6-di-*tert*-butyl-phenol and 2,4-di-*tert*-butylphenol with formaldehyde in the presence of a lower aliphatic alcohol having up to 4 carbon atoms under basic conditions.

The make-up of the mixtures of phenols employed in the process of this invention can vary over a wide range. Thus, as high as 93 to 94 mole per cent of a first phenol and 6 to 7 per cent of a second phenol may be employed. Generally speaking however, at least 10 per cent of a single phenolic component having a hydrogen in the ortho or para position or both and a tertiary alkyl group of from 4—9 carbon atoms ortho to the hydroxyl group is employed. Thus, mixtures of from 10—50 per cent of a first phenol and 50—90 per cent of a second phenol are employed. In a preferred embodiment of this invention the mixture of phenols always contains at least 50 per cent of a 2,6-dialkylphenol in which one of the alkyl groups is a tertiary alkyl group as defined above, most preferably a tertiary butyl group.

The lower aliphatic alcohol employed in the process of this invention has from 1 to 4 carbon atoms. However, those having from 2—4 carbon atoms, i.e., ethanol, propanol, and isopropanol are preferred since highly effective and readily soluble products are prepared by employing these. Methanol may also be employed in the process of this invention but the yield of asymmetric methylene-bis-phenols is somewhat reduced due to the formation of a higher percentage of methylols.

A preferred embodiment of this invention comprises reacting the mixture of phenols, ethanol and formaldehyde in the presence of a base under essentially anhydrous conditions. That is, best results are obtained when the ethanol employed contains up to about 5 per cent water and the other reactants are anhydrous. However, good results are also obtained when additional water is present in the reaction.

The formaldehyde may be employed as the pure compound or as para-formaldehyde. Formalin (aqueous formaldehyde) may also be employed but since its use introduces excess water to the reaction, other forms of formaldehyde are preferred.

The basic conditions under which the process is conducted are obtained with a strong base preferably sodium or potassium hydroxide. In laboratory preparations, potassium hydroxide is preferred because it is less hygroscopic and has greater solubility in

alcohol. However, sodium hydroxide may preferably be employed in commercial operations and it is preferred since it is more readily available.

5 In general, the reaction is conducted at or near the reflux temperature of the mixture for from about 30 minutes to 6 hours. However, reaction temperatures both substantially below and above the reflux temperature may be employed and reaction times outside this range will also yield desirable products.

10 When the reaction is completed, the mixture should be neutralized with an acid such as glacial acetic acid, the water phase separated and the majority of the excess alcohol stripped from the mixture. Further work-up of the mixture is often desirable and this may be accomplished by diluting with a solvent and washing the mixture with water several times after which the product is dried and the solvent removed by dilution. The following examples illustrate the preparative process of this invention and the products obtained.

EXAMPLE I.

25 In a reaction vessel equipped with reflux condenser, heating means, means for agitating the contents and means for keeping a reaction mass under nitrogen flush was added a solution of 460 parts of 2-methyl-6-*tert*-butylphenol and 103 parts of 2,6-di-*tert*-butylphenol in 1184 parts of absolute ethanol. The reaction mixture was stirred and then flushed with nitrogen. About 500 parts of 36 per cent formalin followed by 264 parts of sodium hydroxide in 500 parts of water were added to the reaction mixture. The sodium hydroxide was added drop-wise after the formalin had been added to the reaction vessel and the contents brought to reflux temperature. After the addition of all reactants, reflux was maintained for two hours under a continued nitrogen blanket. The reaction mixture was then cooled and neutralized with 50 per cent acetic acid and poured into 10,000 parts of water to remove the alcohol. The aqueous and organic layers were separated and the aqueous layer was extracted with *n*-hexane. The organic portions were then combined, washed twice with water and dried. The hexane solvent was stripped at two milliliters of mercury pressure at 100° C., giving about 10 parts of distillate and leaving about 510 parts of a very viscous amber oil. Infra-red analysis of this oil showed it to contain primarily a mixture of 4,4'-methylenebis-(2,6-di-*tert*-butylphenol), 4,4'-methylenebis-(2-methyl-6-*tert*-butylphenol), (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3'-methyl-5'-*tert*-butyl-4'-hydroxyphenyl)-methane with 3,5-di-*tert*-butyl-4-hydroxybenzylethyl ether, 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, 3-methyl-5-*tert*-butyl-4-hydroxybenzyl ethyl ether and 3-methyl-5-*tert*-butyl-4-hydroxybenzyl alcohol as minor components.

65 Portions of this viscous liquid were dis-

solved at 5, 10 and 20 weight per cent concentrations to a neutral hydrocarbon lubricating oil by heating to 100° C. After standing for three weeks at room temperature, none of these oil solutions showed any precipitate.

70 In the above example the ratio of starting materials was 85 mole per cent of 2-methyl-6-*tert*-butylphenol to 15 mole per cent of 2,6-di-*tert*-butylphenol and it can be seen that a highly soluble product was formed by this mixture. In addition to its highly desirable solubility properties this mixture has an outstanding antioxidant effectiveness. This is shown, for example, by the following test: Some of the mixture was dissolved in pure white refined mineral oil to the extent that 0.496 weight per cent was present in the mineral oil. Ferris hexoate was also added to the mineral oil to catalyze oxidation and make the test more severe. The concentration of the iron salt was adjusted to 0.05 per cent based on Fe₂O₃. One ml. of the resulting composition was charged to an apparatus for measuring the oxidative stability of the mineral oil. The apparatus consists of a glass vessel having a 12 ml. capacity and an inlet tube which can be connected to a mercury manometer. The vessel is flushed with oxygen at atmospheric pressure and then connected to the mercury manometer. It is then immersed in a constant temperature bath at 150° C. whereupon the oxygen pressure rise is indicated on the manometer. The manometer is observed until a rapid pressure drop in the vessel occurs. The time from immersion to initiation of the pressure drop is the induction period of the mineral oil. When mineral oil containing the iron hexoate is subjected to this oxidative test, a pressure drop in the manometer is observed in from 2 to 3 minutes, showing that the mineral oil is unstable to oxidative deterioration at 150° C. However, when the composition containing 0.496 weight per cent of the mixture prepared as shown in Example I, is tested in this fashion, no pressure drop is observed in the manometer until after 172 minutes. When pure 4,4'-methylenebis-(2,6-di-*tert*-butylphenol), an outstanding symmetrical antioxidant, is tested by this procedure, the induction time is 84 minutes.

EXAMPLE II.

A mixture of 75 per cent of 2,6-di-*tert*-butylphenol and 15 per cent ortho-tertiary-butylphenol containing 10 per cent of 2,4,6-tri-*tert*-butylphenol was reacted with para-formaldehyde in the presence of ethanol. The following amounts of reactants were employed:

724 parts of phenol mixture	
20 parts of potassium hydroxide	
76 parts of para-formaldehyde	125
600 parts of 95 per cent ethanol	

The reaction was conducted at reflux (81—83° C.) for two hours after which time the

mixture was cooled to 70° C. and neutralized with glacial acetic acid. The alcohol was stripped under vacuum beginning at 70° C. and ending at 35° C. and 10 mm. pressure.

5 The residue was then dried with 1400 parts of benzene and washed three times in 750 part aliquots of water, dried and the benzene was removed by vacuum distillation. The reaction product, a viscous oil, was found to
10 be completely soluble and miscible with a hydrocarbon lubricating oil at up to 20 per cent weight concentration. The reaction product contains 4,4'-methylenebis-(2,6-di-*tert*-butylphenol), (3,5-di-*tert*-butyl-4-hydroxyphenyl) - (3'-*tert*-butyl-2'-hydroxyphenyl)-methane and (3,5-di-*tert*-butyl-4-hydroxyphenyl) - (3'-*tert*-butyl-4'-hydroxyphenyl)-methane as major components.
15 In addition the reaction mixture contains numerous other possible condensation products of 2,6-di-*tert*-butylphenol and *o*-*tert*-butylphenol such as 4,4'-methylenebis-(2-*tert*-butylphenol), 2,2'-methylenebis-(6-*tert*-butylphenol), (3-*tert*-butyl-2-hydroxyphenyl) - (3'-*tert*-butyl-4'-hydroxyphenyl)-methane, 3-*tert*-butyl-4-hydroxybenzyl ethyl ether, 3-*tert*-butyl-2-hydroxybenzyl ethyl ether, the derivative of *o*-*tert*-butylphenol having ethyl ether substituents on
20 methyl groups ortho and para to the hydroxyl group.

EXAMPLE III.

Potassium hydroxide, 20 parts, para-formaldehyde, 75 parts, and 568 parts of a mixture
35 of 15 mole per cent of 2,6-di-*tert*-butylphenol and 85 mole per cent of 2-methyl-6-*tert*-butylphenol were dissolved in 800 parts of isopropanol. The mixture was heated at reflux for three hours, cooled and then
40 neutralized with glacial acetic acid and quenched in 10,000 parts of water. After phase separation the reaction mixture was diluted with ether to three times volume. After dilution, the mixture was washed three times with
45 water, dried and the solvent was removed. The product was a crystalline solid which is soluble in a neutral mid-continent commercially available lubricating oil.

EXAMPLE IV.

50 In 1250 parts of 95 per cent ethanol was dissolved 663 parts of a mixture of 85 mole per cent of 2,6-di-*tert*-butylphenol and 15 mole per cent of 2-methyl-6-*tert*-butylphenol. To the solution was added 500 parts
55 of a 0.65 mole aqueous formaldehyde solution. The mixture was then heated to reflux and 264 parts sodium hydroxide in 500 parts of water was added slowly to the reaction mixture. After addition of the base, reflux was continued
60 for two hours; the mixture was then cooled and neutralized with acetic acid. The mixture was diluted with about 900 parts of benzene. The aqueous phase was quenched in water and extracted with benzene twice and the combined
65 organic product was washed three times with

water, dried and separated from the solvent by distillation. The product was a solid and was recovered in about theoretical yield.

EXAMPLE V.

Potassium hydroxide, 20 parts, para-formaldehyde, 76 parts, and 665 parts of a
70 mixture of 85 mole per cent of 2,6-di-*tert*-butylphenol and 15 mole per cent of 2-methyl-6-*tert*-butylphenol were dissolved in 600 parts of 95 per cent ethanol. The mixture was heated
75 at reflux for two hours, cooled and neutralized with glacial acetic acid. The majority of the alcohol was then stripped by distillation and the reaction mixture was diluted with 1200 parts of ether as a solvent. The product was washed
80 three times with 750 part aliquots of water, dried and separated from the solvent by vacuum distillation leaving 705 parts of product.

EXAMPLE VI.

The procedure of Example IV was repeated using as the phenol a mixture of 75 per cent of 2,6-di-*tert*-butylphenol and 15 per cent *o*-*tert*-butylphenol containing 10 per cent of 2,4,6-*tri-tert*-butylphenol.
85
90

EXAMPLE VII.

A mixture of equimolar parts of 6-*tert*-amyl-*p*-cresol and 2-methyl-6-*tert*-butylphenol (1,000 parts) is added to 1,000 parts of an equal volume mixture of methanol and isopropanol. 750 parts of 36 per cent formalin followed by 500 parts of sodium hydroxide in 1,000 parts of water was added to the reaction
95 mixture. The base is added slowly after the formalin addition and the mixture is brought to reflux. After addition of all the reactants reflux is maintained for six hours. Work-up of the product is performed as described in Example I. The product contains substantial quantities of (3-*tert*-amyl-5-methyl-2-hydroxyphenyl) - (3'-methyl-5'-*tert*-butyl-4'-hydroxyphenyl)-methane and also contains
100 some 4-methoxy-methyl-2-methyl-6-*tert*-butylphenol and 2-methoxy-methyl-4-methyl-6-*tert*-amylphenol.
105
110

When methanol is employed as a solvent, the formation of benzyl ethers is more pronounced than when the higher alcohols are employed. A small proportion of these ethers is sometimes beneficial in the reaction products of this invention as they aid in increasing solubility. However, since their antioxidant effectiveness is not as great as that of the methylenebis phenols, it is desirable to control their concentration in the final products. Thus, when methanol is employed as a solvent, it is desirable to add some water, ethanol, isopropanol, dioxane, tetrahydrofuran, or other like polar solvent, to maintain a high concentration of phenol and formaldehyde with respect to the methanol. In this way ether formation is kept at a desirable level.
115
120
125

EXAMPLE VIII.

The general procedure of Example II was repeated through the reaction stage. After
130

completion of the reaction, the alcohol was distilled off at atmospheric pressure and the residue was diluted with an equal volume of a neutral additive-free mixed base lubricating oil and heated to 85° C. In this procedure, after the reaction product is completely dissolved in the lubricating oil, the oil solution is washed with water three times and dried. In this manner a final product already dissolved in oil is obtained and a subsequent removal of solvent is rendered unnecessary.

In the above examples the reaction product consists of a mixture of compounds including symmetric methylene-bis-phenols, the novel asymmetric phenols of this invention, benzyl ethers, benzyl alcohols and polymers of various molecular weights. It has been found that these reaction products have excellent solubility properties in organic media. The mixtures are prepared from the mononuclear phenolic compounds described above and ordinarily contain at least about 20 per cent of an asymmetric methylene-bis-phenol of this invention. However, the compositions are also extremely valuable when a lesser quantity of the asymmetric compound is present in the mixture. Thus, an embodiment of this invention comprises a mixture containing about 20 per cent or more of an asymmetric methylene-bis-

phenol as defined above and substantial quantities of symmetric methylene-bis-phenols, benzyl ethers, benzyl alcohols and, when phenols having both an ortho and para position unsubstituted are used as starting materials, some quantity of polymers. The mixtures can contain up to about 50 per cent of an asymmetric methylene-bis-phenol of this invention as a maximum when the two phenols employed have approximately equal reaction rates with formaldehyde and are employed in equimolar ratios. However, in certain instances, it is possible to prepare mixtures having more than 50 per cent of the asymmetric methylene-bis-phenol depending upon the relative reaction rates.

A number of antioxidant compositions of this invention were tested as described above following Example I to show antioxidant effectiveness in pure white mineral oil. The tests employed were identical to that described following Example I in which a quantity of the antioxidant is added to the mineral oil which contains an oxidation catalyst. The oxygen induction time for each sample of the mineral oil containing the antioxidant was determined and the results were summarized in Table I.

TABLE I

Antioxidant Effectiveness in White Mineral Oil

Additive	Concentration — wt. per cent	Induction Time in Minutes
1. None	—0—	2—3
2. Product of Example I	0.496	172
3. Product of Example III	0.496	195
4. Product of Example IV	0.496	125
5. Product of Example V	0.496	122
6. (3,5-di- <i>tert</i> -butyl-4-hydroxy-phenyl)-(3'-methyl-5'- <i>tert</i> -butyl-4'-hydroxyphenyl)-methane	1.00 × 10 ⁻² molar/litre	209

The data in Table I show that all of the compositions of this invention impart excellent antioxidant characteristics to the mineral oil. However, it can be seen that compositions containing a substantial quantity of 2-methyl-6-*tert*-butylphenol get outstanding results. However, the compositions containing substantial proportions of other products are also effective antioxidants and have the marked advantage of being more readily soluble than the pure asymmetric methylene-bis-phenols themselves.

The above data show that products of the process of this invention are outstanding antioxidants. Thus, an embodiment of this invention comprises a composition made up of organic material normally tending to undergo oxidative deterioration in the presence of air, oxygen, ozone or other oxidizing atmosphere containing a small antioxidant quantity, up to 5 per cent, of one or more asymmetric methylene-bis-phenols as hereinbefore defined. An embodiment of this invention comprises the use as antioxidant of an asymmetrical

methylen-bis-phenol as an antioxidant in its pure state. For example, it has been found that (3,5 - di - *tert* - butyl - 4 - hydroxyphenyl) - (3' - methyl - 5' - *tert* - butyl - 4'-hydroxyphenyl)-methane is an outstanding antioxidant in a very large variety of organic media.

The compositions of this invention find important utility as antioxidants in a wide variety of oxygen sensitive materials; thus, liquid and solid products derived from petroleum crude are found to possess greatly increased storage stability by the use of an antioxidant of this invention. For example, gasoline, jet fuel, kerosene, fuel oil, turbine oils, insulating oils, motor oils, and various waxes have increased oxidative stability when they contain an antioxidant of this invention. Likewise, liquid hydrocarbon fuels which contain organometallic additives such as tetraethyl lead and other organometallic compositions which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. Furthermore, such fuels which contain halogen and phosphorus-containing scavengers for these organometallic compounds are benefited by the practice of this invention. In addition to increased storage stability, lubricating oils and functional fluids, such as automatic transmission and hydraulic fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, achieve a high degree of resistance to oxidation during use at elevated temperatures by the practice of this invention. It has been found that lubricating oils may be employed at extremely high temperatures without undergoing oxidative degradation when protected by an antioxidant of this invention. The addition of small quantities of the compositions of this invention to such materials as hydraulic, transformer and other highly refined industrial oils as well as crankcase lubricating oils and lubricating greases prepared from these oils by the addition of metallic soaps, greatly increase their resistance to deterioration in the presence of air, oxygen or ozone. Furthermore, the organic soaps used in the preparation of lubricating greases are themselves stabilized by the practice of this invention.

Organometallic compositions such as tetraethyl-lead and tetraethyl lead antiknock fluids containing halo-hydrocarbon scavengers, dyes and which may contain various phosphorus compounds and other organometallic additives are stabilized against deterioration during storage by the addition thereto of an antioxidant quantity of the compositions of this invention.

The compositions of this invention are also extremely effective antioxidants for elastomers including high molecular weight unsaturated hydrocarbon polymers both derived from naturally occurring sources and those synthetically prepared. Thus, natural rubbers and

synthetic rubbers, including oil extended rubbers, are greatly benefited by the practice of this invention. Examples of the synthetic rubbers protected by the practice of this invention include such synthetics as polybutadiene, methyl rubber, polybutadiene rubber, butyl rubber, GR-S rubber, GR-N rubber, piperylene rubber and dimethylbutadiene rubber.

The practice of this invention is also useful in protecting paraffin and micro-crystalline petroleum waxes against the oxidative deterioration which leads to rancidity. Furthermore, the compositions of this invention are extremely useful in the stabilization of fats and oils of animal or vegetable origin which become rancid during periods of storage due to oxidative deterioration. Typical animal fats benefited by the practice of this invention include butter fat, lard, beef tallow, fish oils—such as cod liver oil—as well as various foods containing or prepared in animal fats which tend to deteriorate. These include, for example, potato chips, fried fish, doughnuts, crackers, and various types of pastry such as cakes and cookies. Furthermore fat fortified animal feeds and fish meals used as animal feeds are greatly benefited by the practice of this invention. Not only are these compositions protected against oxidative deterioration but the inclusion of a composition of this invention in such materials inhibits the degradation of vitamins A, D and E and certain of the B complex vitamins. Examples of compositions containing oils derived from vegetable sources which are benefited by the practice of this invention include castor oil, soy bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, citrus oils, cotton seed oil and various compositions containing these including peanut butter, peanuts and other whole nuts, salad dressings, margarine and other vegetable shortenings.

The compositions of this invention are also outstanding antioxidants for various organic compounds and polymeric materials including polystyrene, polyvinylchloride, polyvinyl acetate, various epoxide resins and polyester resins and polymers including the alkyls. However, in particular the compositions of this invention are outstanding antioxidants for saturated hydrocarbon synthetic polymers derived from polymerization of an aliphatic monoolefin hydrocarbon compound having preferably up to 4 carbon atoms and only a single unit of unsaturation per monomeric molecule. Examples of such monomers include ethylene, propylene, butylene and isobutylene. Thus the polymers are homopolymers and copolymers of ethylene, propylene, butylene and isobutylene and are usually solid. Polyethylene and polypropylene are preferred polymers in the practice of this invention and they are derived from the polymerization of ethylene and propylene respectively. This polymerization

can be accomplished by a great variety of methods which lead to products of diverse properties. The polymers which are employed may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerization - favouring quantities of oxygen under relatively high pressures in excess of 500 or 1,000 atmospheres at temperatures between 150 and 275° C. or they may be the essentially linear and unbranched polymers ordinarily having greater molecular weights obtained under relatively low pressures of 1 to 100 atmospheres by polymerization of ethylene or propylene using such catalysts as mixtures of strong reducing agents and compounds of Groups IVB, VB and VIB metals of the Periodic System; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt. The polymers which result from these various polymerization processes may have a molecular weight in the range from 1300 to over 1,000,000 depending on the particular conditions of polymerization employed. However, they are usually solids having molecular weights over 10,000. Whereas all of the above mentioned organic compositions are greatly benefited by the practice of this invention, the preferred embodiments of this invention are those directed to lubricating oils, functional fluids and saturated hydrocarbon polymers such as polyethylene and polypropylene. Although the problems involved in stabilizing these compositions against oxidative deterioration are not equivalent, it has been found that the compositions of this invention give superior results in all of these compositions, probably due to the asymmetric nature of the additives.

The following examples are illustrative of the compositions of this invention and their preparation.

EXAMPLE IX.

To 1,000 parts of polyethylene produced by oxygen catalyzed reaction under a pressure of 20,000 atmospheres having an average molecular weight of about 40,000, is added and mixed by milling on hot rolls 2 parts of (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3¹-methyl-5¹-*tert*-butyl-4¹-hydroxyphenyl)-methane. The resulting composition has greatly increased oxidative stability. Excellent results are also obtained when similar quantities of (3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-(3¹,5¹-dimethyl-4¹-hydroxyphenyl)-methane or (3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-(3¹,5¹-diisopropyl-4¹-hydroxyphenyl)-methane are employed.

EXAMPLE X.

To a master batch of high molecular weight polyethylene having an average molecular weight of about 1,000,000, a tensile strength of about 6,700 psi, a Shore D hardness of 74 and a softening temperature under low load of 150° C. is added 5 per cent of a mixture

of phenols prepared from 2,6-di-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol as described in Example I. Polyethylene of greatly improved oxidative stability results. Similar results are also obtained when other mixtures containing asymmetric phenols of this invention are employed.

EXAMPLE XI.

To a wax-like polypropylene having a melting point in excess of 130° C., a molecular weight of about 4,000 and a density of 0.913 is added 3 per cent of the mixture of methylene-bis-phenols produced as shown in Example II. The phenolic mixture is added to the polypropylene in the molten state and the mixture is allowed to solidify into the desired shape. A polypropylene product of outstanding oxidative stability results.

EXAMPLE XII.

Linear polyethylene having a high degree of crystallinity (up to 93 per cent) and less than one ethyl branch chain per 100 carbon atoms, a density of about 0.96 and about 1.5 double bonds per 100 carbon atoms is treated with 50×10^{-4} roentgens of beta radiation. To the thus treated polymer is added 0.01 per cent of (3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-(3¹,5¹-di-*tert*-butyl-4¹-hydroxyphenyl)-methane and the resulting product has greatly improved oxidation stability characteristics due to the presence of the asymmetric phenol of this invention.

EXAMPLE XIII.

To a polyisobutylene polymer having an average molecular weight of 35,000 is added a sufficient quantity of the phenolic mixture prepared as shown in Example I from 2,6-di-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol, to give a composition containing 0.1 per cent of the antioxidant. This composition has improved anti-oxidant properties due to the presence of the phenolic mixture containing the asymmetric methylene-bis-phenol of this invention.

In addition to the asymmetric methylene-bis-phenol containing an antioxidant of this invention, the saturated hydrocarbon polymers may contain other compounding and colouring additives including carbon black, elastomers, polyvinyl compounds, carboxylic acid esters, urea-aldehyde condensation products, flame retarding agent such as antimony trioxide and chlorinated hydrocarbons and various pigment compositions designed to impart color to the finished product.

EXAMPLE XIV.

To a synthetic rubber master batch consisting of 100 parts of GR-S rubber having an average molecular weight of about 65,000, 50 parts of mixed zinc propionate stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulphur and 1.5 parts of mercaptobenzothiazole, is added 3 parts of (3-methyl-5-*tert*-octyl-4-hydroxyphenyl)-(3¹,5¹-di-*tert*-butyl-4¹-hydroxyphenyl)-

methane. This batch is then cured for one hour at 45 psi of steam pressure to give a rubber having excellent antioxidant properties.

EXAMPLE XV.

- 5 One part of a liquid mixture prepared from equimolar mixture of 2,6-di-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol according to the procedure outlined in Example I, which mixture contains a substantial portion of (3,5-di-*tert*-butyl-4-hydroxyphenyl)-(3-methyl-5-*tert*-butyl-4-hydroxyphenyl)-methane, is blended with the following rubber composition and vulcanized for 60 minutes at 280° F. to produce a highly oxidative resistant natural rubber stock: 100 parts of thick gristly crepe natural rubber, 2 parts of wax, 0.1 part of ultramarine dye, 70 parts of zinc oxide, 20 parts of titanium dioxide, 3 parts of sulphur, 1.2 parts of stearic acid, 0.4 parts of benzothiazyl disulphide and 0.5 parts of amine activator.

- 15 In adding an antioxidant of this invention to a mineral lubricating oil, it is often advisable to heat the oil to from up to about 100° C. and agitate the oil while adding the antioxidant. This method is ordinarily resorted to to obtain a homogenous composition having the antioxidant well dispersed.

- 20 The lubricating oils used in the practice of this invention include those fractions or blends of fractions from mineral oils which are used for lubricating purposes in the crankcase of an internal combustion engine. Lubricating oil stock is usually considered to include all the distillate obtainable from crude oils after the lower boiling fractions and case oils have been expelled as well as some of the residues that are left in the still when known asphalt crudes are distilled. Generally, lubricating oils are made from distilled fractions of the crude, but often these distilled fractions are combined with refined residuum, such as bright stocks, to yield oils having excellent lubricating qualities. In addition to the antioxidant of this invention, the lubricating oil may contain other additives. These other additives may include, for example, viscosity index improvers, detergents, corrosion inhibitors, metal deactivators, rust inhibitors, color stabilizers, pour point depressants, emulsifiers and dyes.

- 50 The finished lubricants of this invention have much greater oxidative stability and many other improved performance characteristics as compared with the corresponding base oils. To further illustrate some of the properties of the novel compositions of this invention, recourse is had to the Polyveriform Oxidation Stability Test as described in the paper entitled "Factors Causing Lubricating Oil Deterioration in

Engines" (Ind. and Eng. Chem. Anal. Ed., 17, 302 (1945)). See also "A Bearing Corrosion Test for Lubricating Oils and Its Correlation with Engine Performance" (Anal. Chem., 21, 737 (1949)). This test effectively evaluates the performance of lubricating oil antioxidants. The test equipment procedure employed and correlations of the results with engine performance are discussed in the first paper above cited. By employing various compositions of this invention in oxygen-sensitive lubricating oil, effective inhibition of oxidative deterioration is achieved.

Tests conducted using the method and apparatus essentially as described in the publication first above mentioned show the benefits obtained by the additives of this invention. One minor modification was that the steel sleeve and copper test piece described in this publication were omitted from the apparatus. In these tests a neutral mineral crankcase oil consisting of mixed base and no additive was used. The principal test conditions consisted of passing 70 liters of air per hour through the test oil for a total period of 20 hours while maintaining the oil at a temperature of 300° F. The 300° temperature was employed in these tests to show that the antioxidants of this invention are outstanding even at greatly elevated temperatures. It has been found in practice that many compounds which exhibit antioxidant properties at 280° F. fail the Polyveriform Test at 300°. The transition from 280 to 300° F. therefore represents a critical test of the usefulness of an antioxidant in lubricating oil. Oxidative deterioration of the oil was further promoted by employing as oxidation catalysts 0.05 per cent by weight of ferric oxide (as ferric 2-ethyl-hexanoate) and 0.10 per cent by weight of lead bromide, both of these amounts being based upon the weight of oil employed. Lubricating oils of this invention were then prepared by blending individual samples of the above oil with compositions prepared by the process of this invention. These compositions were then subjected to the above stringent oxidation test. The results of these tests are shown in Table II.

The data in Table II clearly indicate that excellent results are obtained by using the compositions of this invention. Thus, in each test a very great reduction in acid number and viscosity increase was achieved by the compositions of this invention. Furthermore, the visual sludge rate of the oils was in every case improved by the addition of 1 per cent of a composition prepared by the process of this invention.

TABLE II
Polyveriform Test Data

Additive	Concentration in wt. per cent	Acid No.	Per Cent Viscosity Increase (SUS at 100°F.)	Visual Sludge Rating
1. None	—0—	6.0	103	B
2. (3,5-di- <i>tert</i> -butyl-4-hydroxy-phenyl)-(3 ¹ -methyl-5 ¹ - <i>tert</i> -butyl-4 ¹ -hydroxyphenyl)-methane	1.0	3.7	64	A
3. Product of Example II	1.0	5.0	64	A
4. Product of Example III	1.0	4.8	58	A
5. Product of Example V	1.0	4.9	56	A
6. Product of Example VI	1.0	4.7	73	A

In evaluating the improved lubricants of this invention, engine tests are used to demonstrate the reduced engine wear characteristics and greatly improved oxidation stability of the oil as well as greatly reduced bearing corrosion properties. A preferred series of tests is with the single cylinder CLR oil test engine using CRC test designation L—38 with certain minor modifications. The L—38 test is completely described in a pamphlet published by the Motor Oil Oxidation Test Group of the Motor Vehicle, Fuel, Lubricant and Equipment Research Committee of the Coordinating Research Council Inc. The tests were conducted on a straight mineral oil containing no additives which had an SAE viscosity of 20. In addition to a test on the mineral oil without additives, a test was conducted using one half weight per cent of the product of Example II. The test technique involves the continuous operation of the single cylinder CLR oil test engine under constant speed, air-fuel ratio and fuel-flow conditions for a total of at least 40 hours, subsequent to a break-in period of 4½ hours. Prior to each test run, the engine is thoroughly cleaned, measurements of certain engine parts are taken and a new set of piston rings and new copper lead connecting rod test

bearing inserts are installed. Performance of the test oil is judged by a visual examination of the engine for deposits, by the weight loss of the copper lead test bearing and by a comparison of the inspection data on samples of used oil taken at periodic intervals with the inspection data on the new oil. These inspection data consist of the viscosity at 100° F., the acid number and a visual rating of the oil.

For the following tests certain modifications were made in the L—38 test procedure as outlined in the publication described above. The oil sump was operated at 280° F. and a constant engine speed of 3075 RPM was employed. A bronze camshaft thrust washer was employed instead of the aluminum washer called for. The fuel employed in the test was a mixture of 60 per cent alkylate and 40 per cent of a commercially available base stock with 3 ml. of tetraethyl lead per gallon as 62 mix. The "off gas" — that is, the total of blowby and air bled into the crankcase — was not measured. The results of these tests show that the base oil is greatly improved by the addition thereto of one half weight per cent of the product of Example II. This is shown by the data in Table III summarizing the test results.

TABLE III
L—38 Test Results

Additive	Concentration	Bearing wt. loss (MG)	Oil After 40 Test Hours	
			Acid No.	Viscosity Increase per cent
None		1828	3.1	10.9
Product of Example II	0.5 wt. per cent	139	2.0	6.4

The results of these tests as shown in Table III indicate a much more highly stable oil and vastly reduced bearing weight loss result from employing a composition of this invention.

5 The compounds of this invention are particularly effective antioxidants for use in steam turbine oils. This is demonstrated by making use of the standard test procedure of the American Society for Testing materials bearing ASTM designation D-943-54. According to this test procedure, 300 ml. of a suitable test oil is placed in contact with 60 ml. of water and the resulting oil-water system is maintained at a temperature of 95° C. while passing oxygen there-through at a rate of three liters per hour. Oxidation is catalyzed by the use of iron and copper wire. Periodically measurements are made of the acid number of the test oil and failure of an antioxidant is indicated by an acid number in excess of 2.0. It is found that when the various compositions of this invention are added in small antioxidant quantities to steam turbine oils, substantial resistance against oxidative deterioration results.

10 The compounds of this invention are very effective antioxidants for grease. The potency of the compounds of this invention in this respect is demonstrated by conducting the Norma Hoffman Grease Oxidation Stability Test, ASTM Test Procedure D-942-50. It is found that the presence of minor proportions of the compounds of this invention in conventional greases greatly inhibits oxidative deterioration. By way of example an initially antioxidant-free lithium base grease is modified to the extent that it contains 0.5 per cent by weight of the product of Example VIII, and is subjected to the above oxidation stability test. It is found that the presence of the composition produced by the process of this invention greatly retards oxygen absorption by the grease.

15 The compounds of this invention are outstanding antioxidants for synthetic oils, particularly diester oils of the type described in "Industrial and Engineering Chemistry", 39, 481-91 (1947). Thus, the compounds of this invention can be used to very effectively stabilize diesters formed by the esterification of straight-chain dibasic acids containing from 4 to about 16 carbon atoms with saturated aliphatic monohydric alcohols containing from 1 to about 10 carbon atoms. Generally speaking, diester lubricants that are prepared from branched chain alcohols and which have molecular weights ranging from about 300 to about 600 are especially effective lubricants and are very effectively stabilized by the compounds of this invention. Thus, in the diester lubricant embodiments of this invention, use can be made of oxalates, malonates, succinates, adipates, pimelates, suberates, azelates or sebacates.

65 To demonstrate the outstanding utility of

the compounds of this invention in diester lubricants, a series of Panel Coking tests are conducted. The Panel Coking apparatus (described in "Lubrication", 10 No. 4 (1954)) is used to qualify synthetic lubricants for jet engines. The method involves the splashing of a lubricant onto a heated aluminum panel which is maintained at a controlled temperature. The weight of deposit formed on the panel is a measure of the oxidation stability of the lubricant. A stringent test consists of operating the panel at a temperature of 600° F. for 10 hours and allowing the splasher to operate for 5 seconds out of each minute. In tests of this nature, the compounds of this invention give an unusually low deposit weight on the panel.

70 The compounds of this invention very effectively enhance the oxidation resistance of such diester oils as diethyl oxalate; di-*sec*-butyl malonate; di-(2-hexyl) succinate; di-(isohexyl) pimelate; di-(3-decyl) suberate; di-*sec*-amyl glutarate; di-(isobutyl) glutarate; di-(2-ethylbutyl) glutarate; di-(2-ethylhexyl) glutarate; di-*sec*-amyl adipate; di-(3-methylbutyl) adipate; diethyl adipate; di 2-ethylhexyl adipate; di-*sec*-amyl azelate; di-(isobutyl) azelate; di-(2-ethylhexyl) azelate; di-*sec*-amyl sebacate; di-*sec*-butyl sebacate; di-(2-ethylhexyl) sebacate; the glutarates, adipates, azelates and sebacates of branched chain secondary alcohols, such as undecanol and tetradecanol, and in general diesters of the type described in the literature as useful for synthetic lubricant purposes.

100 The compositions of this invention are extremely useful as additives to automatic transmission fluids. By employment of these compositions in automatic transmission fluids, great reductions in the amount of sludge and varnish in the transmission are achieved. Furthermore, the stability of the transmission oil is greatly increased. Automatic transmission fluids ordinarily contain substantial proportions of a refined mineral lubricating oil having carefully selected viscosity characteristics. To fulfil these requirements, the oil is usually distillate oil lighter than an SAE 10 grade motor oil. In addition automatic transmission fluids contain a pour point depressant, a viscosity index improver and may contain various amounts of depressants, so-called anti-squawk agents and various other additives. Transmission fluids containing all of these are greatly benefited by the practice of this invention.

110 To show the benefits of the practice of this invention in automatic transmission fluids, a series of transmission tests is conducted. The equipment used is a standard modern automatic transmission in which the transmission input shaft is driven at 1800 RPM under no load conditions by an electric motor. The oil sump temperature is controlled at 300° F. by means of a transmission water cooled heat ex- 130

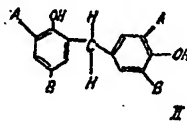
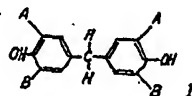
changer. The transmission is continuously cycled between a third and fourth gear so that the shift from third to fourth gear occurred every eight seconds. Thus, during each cycle the transmission is in third gear for four seconds and in fourth gear for four seconds. This cycling was accomplished by means of an Eagle multipulse timer utilizing a synchronous motor driven cam which activates a micro-switch and provides a precise eight second signal to the transmission-shifter arm-air-cylinder-solenoid valve. The transmission displaces approximately one quart of fluid from a fluid coupling in the transmission during the shift from third to fourth gear. The displaced fluid is replaced by an equal quantity of air which is taken in and expelled from the transmission case through a vent. Thus, during the test, the fluid is in constant contact with air and is, therefore, much more subject to breakdown and deterioration than a fluid operating in a closed transmission system having no access to air. Each test is carried out for a total of 120 hours. A sample of the transmission fluids is taken every 24 hours for inspection. On completion of the test, the transmission is dismantled and various operating parts are visually inspected for sludge and varnish. The stability of the test oil before, during and after the test is determined by means of used oil analyses. The properties checked are the viscosity increase of the oil and the change in acid number during the test procedure. Tests of this nature conducted on an automatic transmission base fluid containing a substantial proportion of a mineral lubricating oil and a viscosity improver and pour point depressant show conclusively that the compounds and compositions of this invention are extremely effective antioxidants in automatic transmission fluids.

Additional outstanding uses of the compounds of this invention involves their use in steam turbine oils, greases, synthetic oils, particularly diester oils of the type described in "Industrial and Engineering Chemistry" 39, 481-491 (1947), and automatic transmission fluids.

We are aware of the Public Health (Preservatives etc. in Food) Regulations, 1925-1953, and in so far as our invention relates to the manufacture for sale in the United Kingdom and/or sale in the United Kingdom of foodstuffs preserved by the process herein described, we make no claim to use the invention in contravention of the law.

WHAT WE CLAIM IS:—

1. Asymmetric methylene-bis-phenols having the general formula:



wherein A and B are hydrogen atoms or alkyl groups having up to 9 carbon atoms and wherein at least one A or B is a tertiary alkyl group having from 4 to 9 carbon atoms and is positioned ortho to one of the hydroxyl groups, and when the hydroxyl groups are both para to the methylene bridge A and B are such that the molecule is not symmetrical.

2. A process of preparing asymmetric-methylene-bis-phenols having the general formulae set forth in claim 1 (in admixture with symmetrical methylene-bis-phenols compounds) which comprises reacting a mixture of mononuclear phenols with formaldehyde and an aliphatic alcohol, said mixture containing at least one phenol having an available hydrogen in the ortho or para position and at least one phenol having a tertiary alkyl group ortho to the hydroxyl group and also an available hydrogen in the ortho or para position, the reaction being carried out under basic conditions.

3. The process according to claim 2, wherein the alkyl phenols are ortho-*tert*-butylphenol and 2,6-di-*tert*-butylphenol.

4. The process in accordance with claim 2, wherein the mononuclear phenols are ortho-*tert*-butylphenol, 2,6-di-*tert*-butylphenol and 2,4,6-di-*tert*-butylphenol.

5. The process according to claim 2, wherein the mononuclear phenols are 2-methyl-6-*tert*-butylphenol and 2,6-di-*tert*-butylphenol.

6. (3,5 - Di - *tert* - butyl - 4 - hydroxyphenyl) - (3¹ - *tert* - butyl - 4¹ - hydroxyphenyl)-methane.

7. (3,5 - Di - *tert* - butyl - 4 - hydroxyphenyl) - (3¹ - methyl - 5¹ - *tert* - butyl - 4¹ - hydroxyphenyl)-methane.

8. Organic material normally tending to deteriorate in the presence of air, oxygen or

ozone, stabilized against such oxidation by the inclusion therein of a small anti-oxidant quantity of one or more asymmetric methylene-bis-phenols according to claims 1, 6 or 7.

- 5 9. Organic material according to claim 3, including up to 5% of said asymmetric methylene-bis-phenols.

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